OPERANDO SYNTHESIS OF MACROPOROUS MOLYBDENUM DISELENIDE FILMS FOR ELECTROCATALYSIS OF THE HYDROGEN-EVOLUTION REACTION

FADL H. SAADI[1,2], AZHAR I. CARIM[3], JESUS M. VELAZQUEZ[2,3], JACK H. BARICUATRO[2,3], CHARLES C. L. MCCRORY[2, 3], MANUEL P. SORIAGA[2,6,7], AND NATHAN S. LEWIS[2–5, 7]

[1]Division of Engineering and Applied Sciences

[2]Joint Center for Artificial Photosynthesis

[3]Division of Chemistry and Chemical Engineering

[4]Beckman Institute

[5]Kavli Nanoscience Institute

California Institute of Technology

Pasadena, CA 91125

[6]Department of Chemistry

Texas A&M University

College Station, TX 77843

[7]Corresponding authors. E-mail addresses: m-soriaga@tamu.edu, nslewis@caltech.edu

Physical Characterization

High-Resolution Transmission Electron Microscopy (HRTEM)

HRTEM was performed with a Tecnai F30ST system (FEI, Hillsboro, OR) run at a voltage of 300 kV. The films were prepared by pipetting the particle suspension onto 300-mesh carbon-coated Cu grids and allowing the suspension to evaporate.

X-Ray Diffraction (XRD)

XRD measurement patterns were recorded on a Bruker D8 Discover with Vantec500 area detector using Cu Kα radiation (λ = 1.5418 Å) at 50W. XRD was performed on a powder of molybdenum selenide that was synthesized by drying the precipitant of the centrifuged products.

Faradaic Efficiency Calculations

Chronopotentiometric data from the stability studies show that the total number of electrons passed in 24 hours at 10 mA cm^{-2} is 1.75 x 10^{-3} mol of electrons. Assuming a competing $2e^-$ process involving all the Mo atoms in the film [e.g. the reduction of Mo(VI) to Mo(IV)], only 1.1 x 10^{-6} mol of e^- would be consumed; thus, the current associated with this side reaction is less than 0.1% of the total measured current. Even in the extreme hypothetical case of a competing $6e^-$ process, the side reaction would still constitute less than 0.2% of the total measured current. Hence, the faradaic yield is greater than 99%.

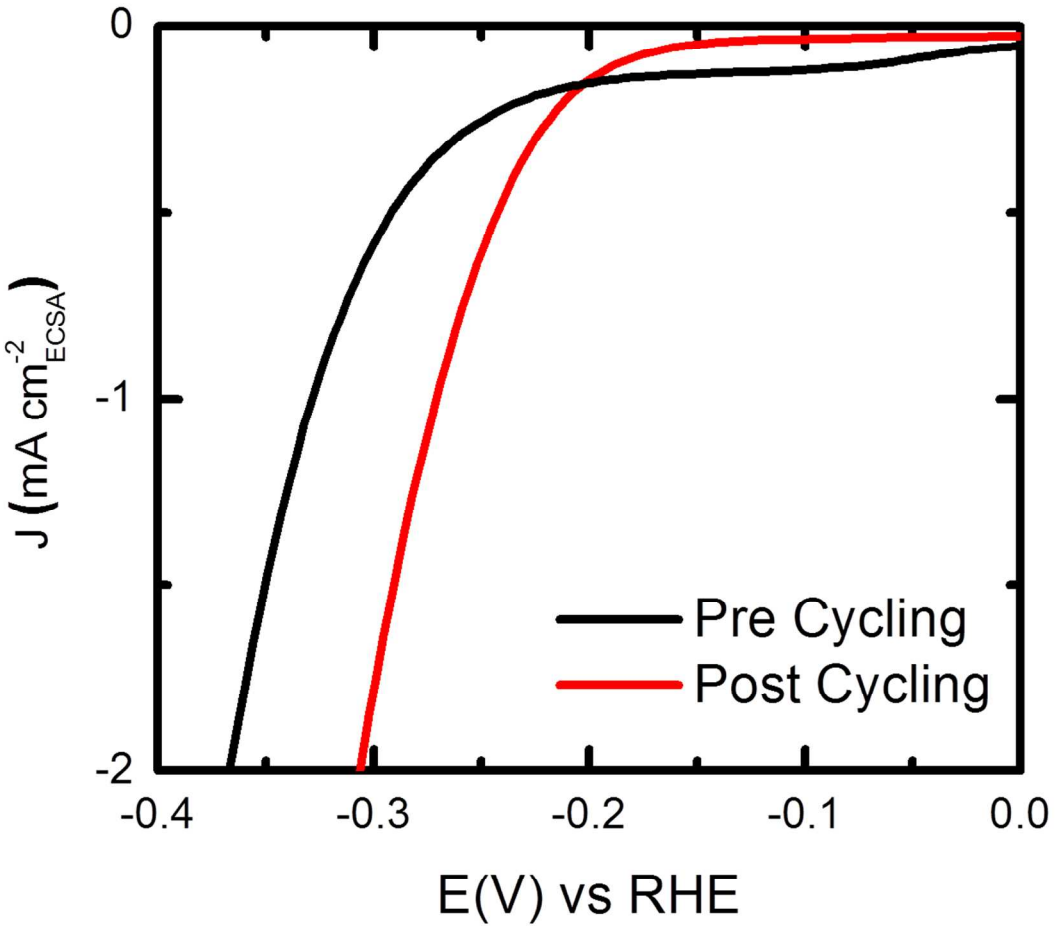

Figure S1. Current density-potential profile of the prepared film before (pre-cycling) and after (post-cycling) electrolysis. Normalization of the current density to the electrochemically active surface area gives rise to two distinct polarization curves that show fundamental differences in the catalytic activity of $MoSe_3$ and $MoSe_2$.

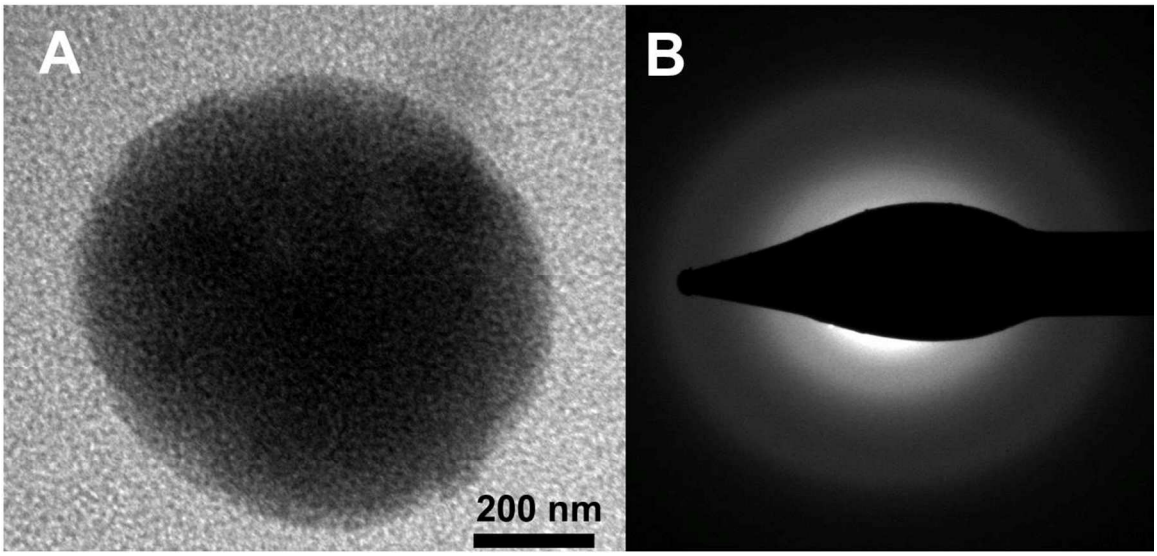

Figure S2. (A) High-resolution transmission electron micrograph of an isolated molybdenum selenide nanoparticle. (B) Selected area electron diffraction pattern of a molybdenum selenide nanoparticle. The absence of Moiré fringes indicates the amorphous nature of the material as synthesized.

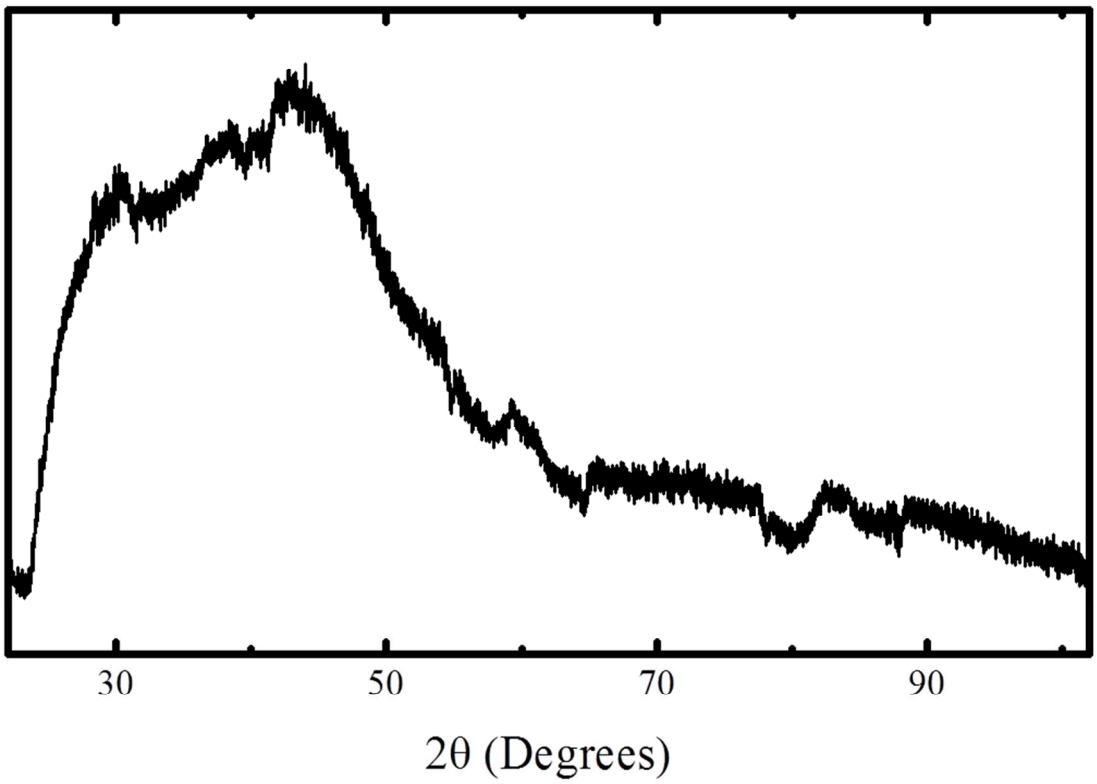

Figure S3. X-ray diffraction of as-synthesized molybdenum selenide powder. The absence of distinct diffraction peaks suggests a lack of crystallinity.

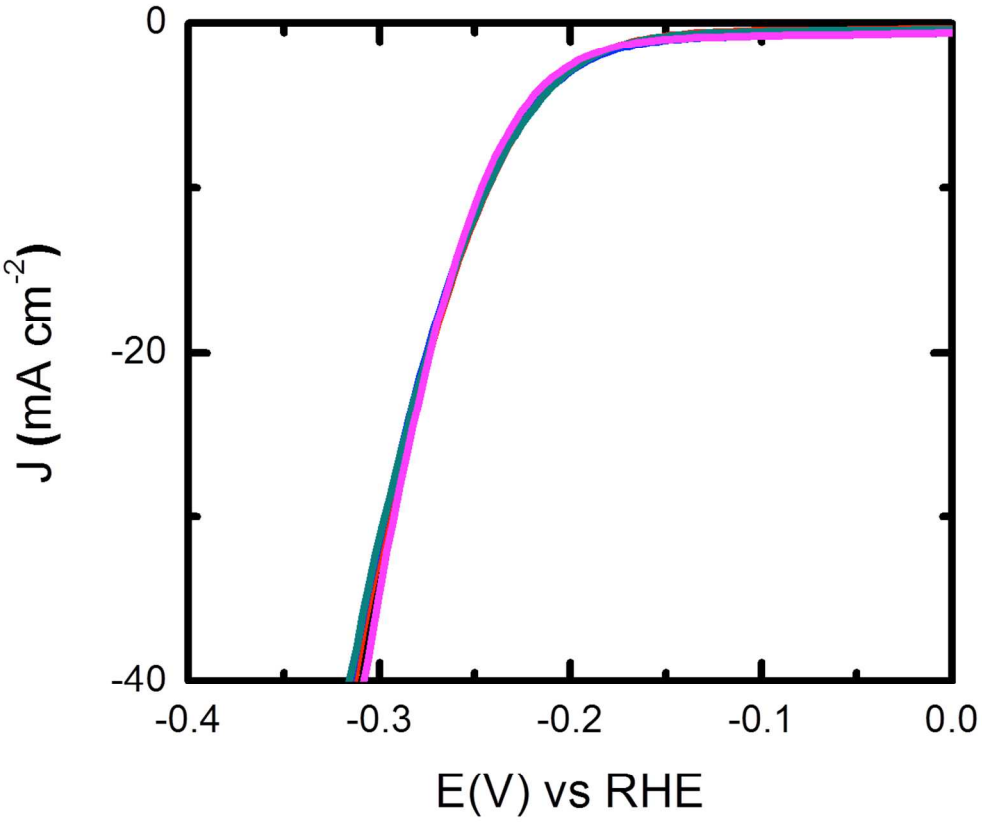

Figure S4. Linear sweep voltammagrams, taken after the tenth scan, of five different molybdenum selenide samples in 0.1 M H_2SO_4. Overpotentials to run 10 mA/cm^2 differ by less than 5 mV.

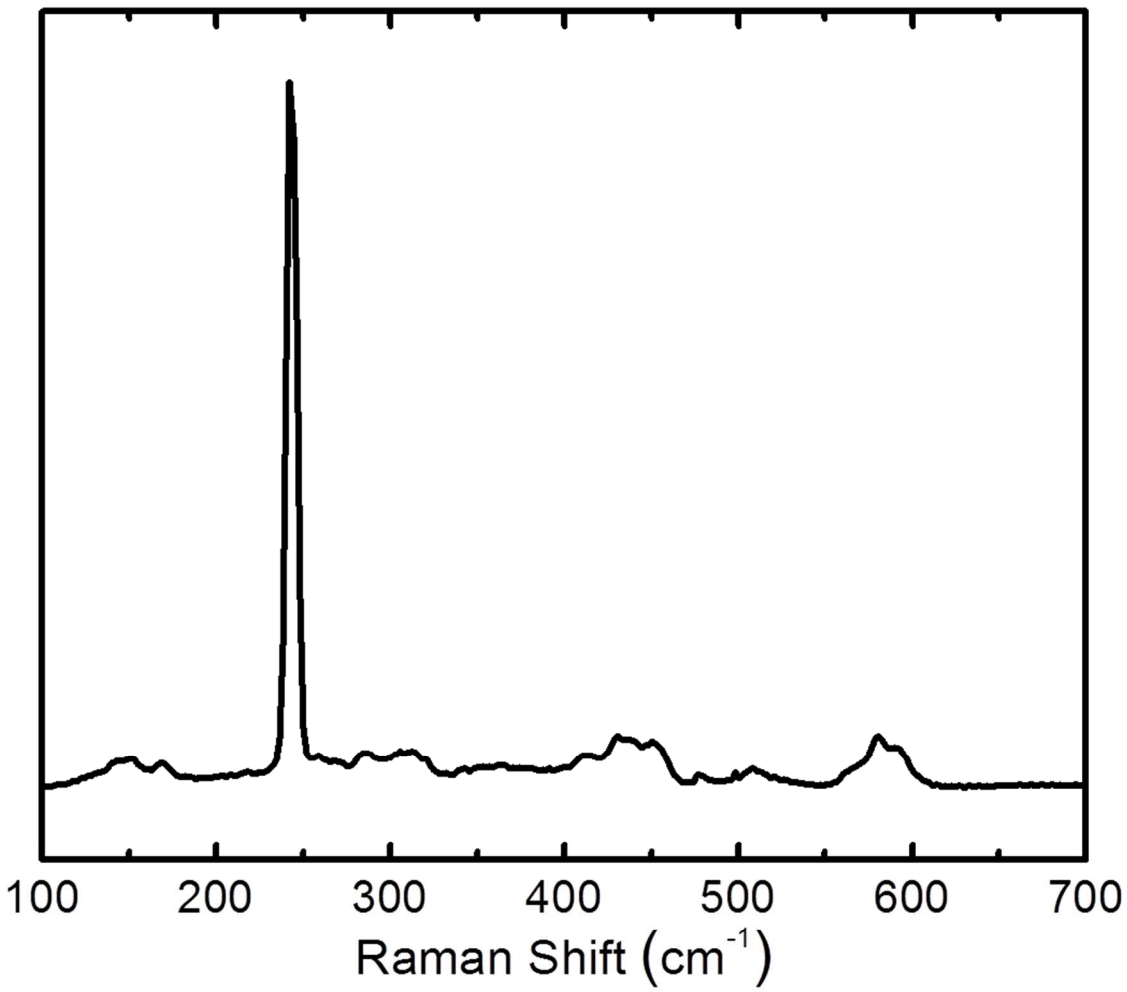

Figure S5. Raman spectrum of a molybdenum selenide single crystal.

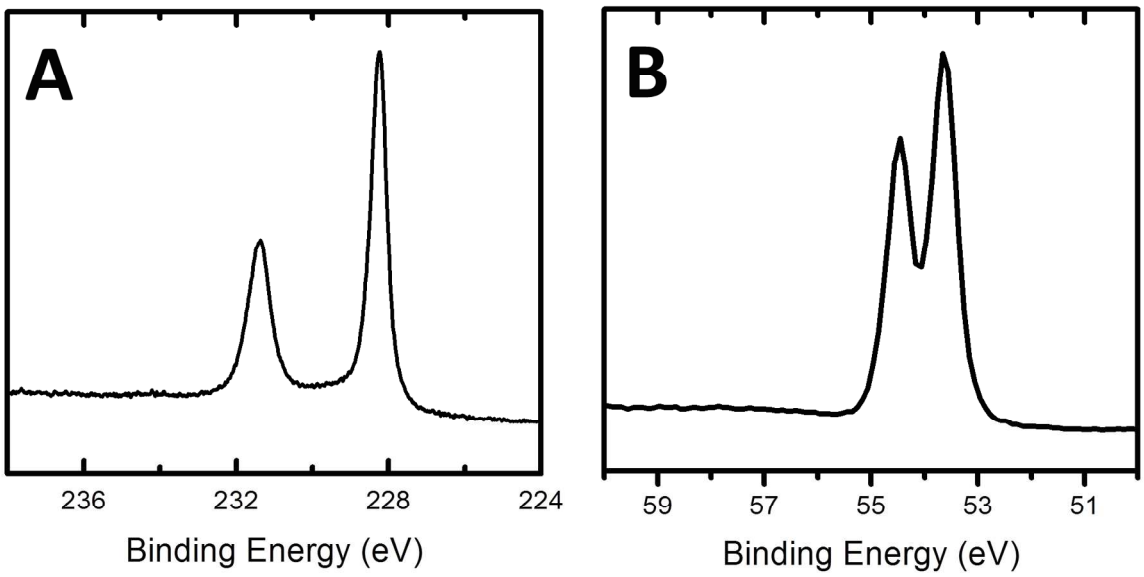

Figure S6. X-ray photoelectron spectra of $MoSe_2$ single crystal: (A) Mo 3d and (B) Se 3s regions.

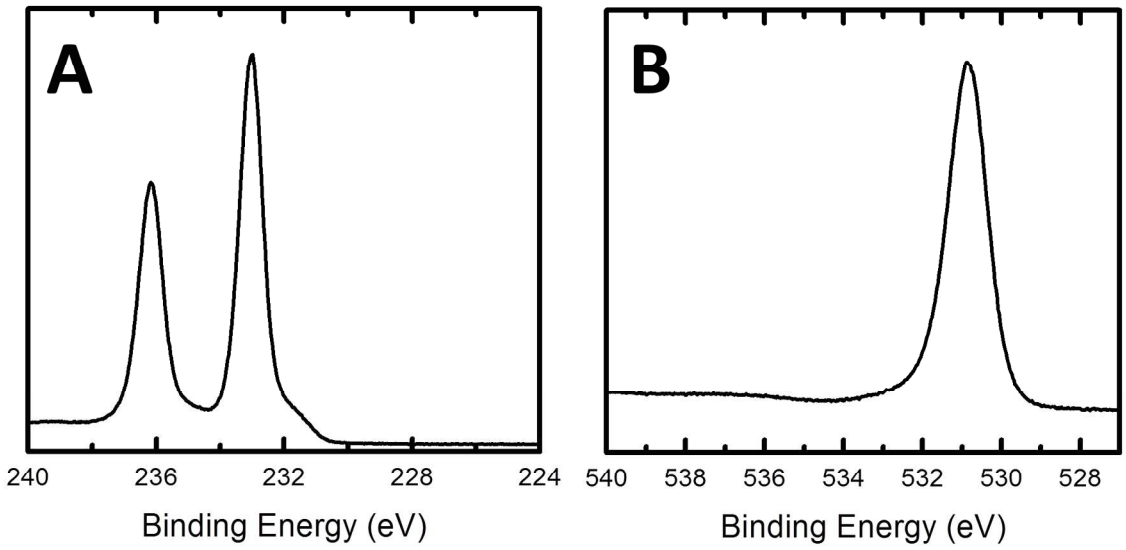

Figure S7. X-ray photoelectron spectra of MoO_3: (A) Mo 3d and (B) O 1s regions.

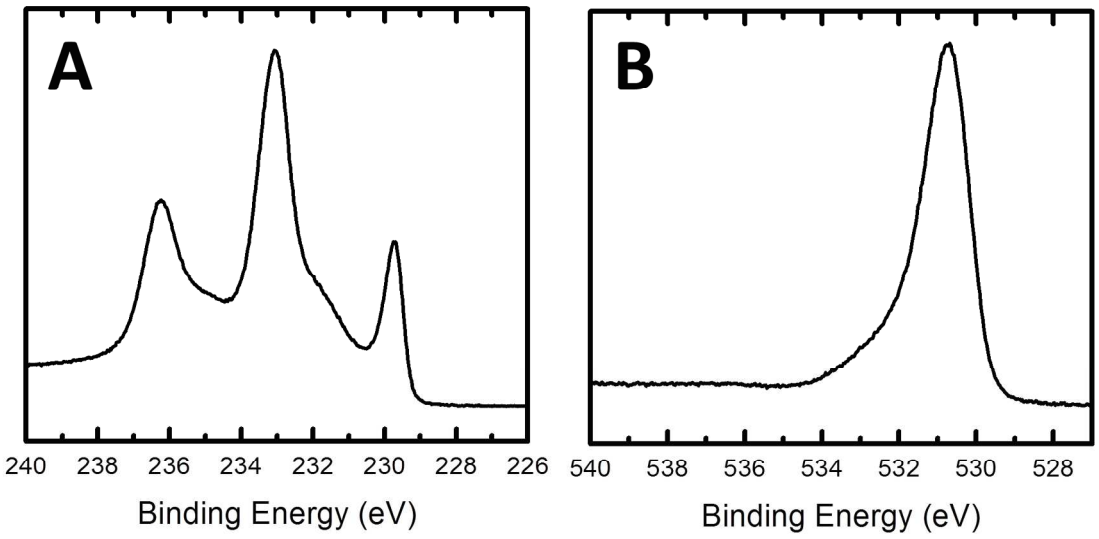

Figure S8. X-ray photoelectron spectra of MoO_2: (A) Mo 3d and (B) O 1s regions. Peaks at 233 and 236 eV are attributed to MoO_3 formed from the air oxidation of the MoO_2 samples.

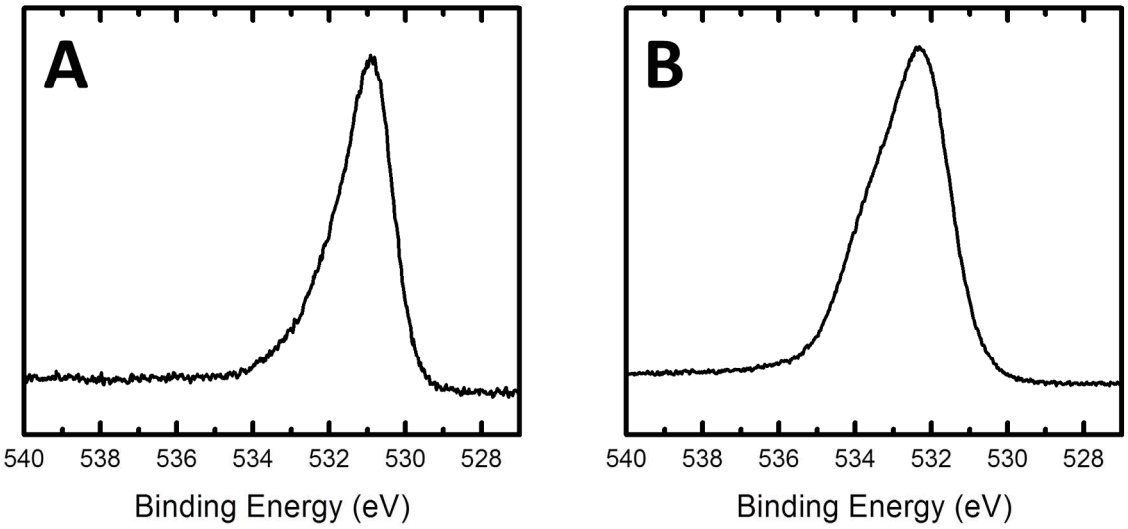

Figure S9. X-ray photoelectron spectra of the O 1s region: (A) As-deposited thin film and (B) after 10 cycles

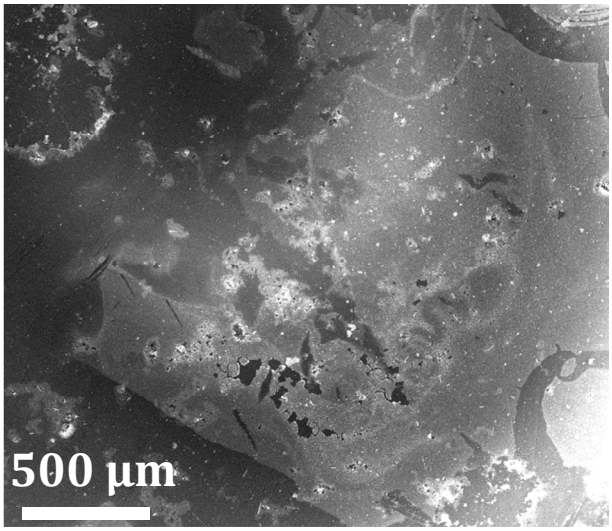

Figure S10. Scanning electron micrograph of the film after 48 hours.

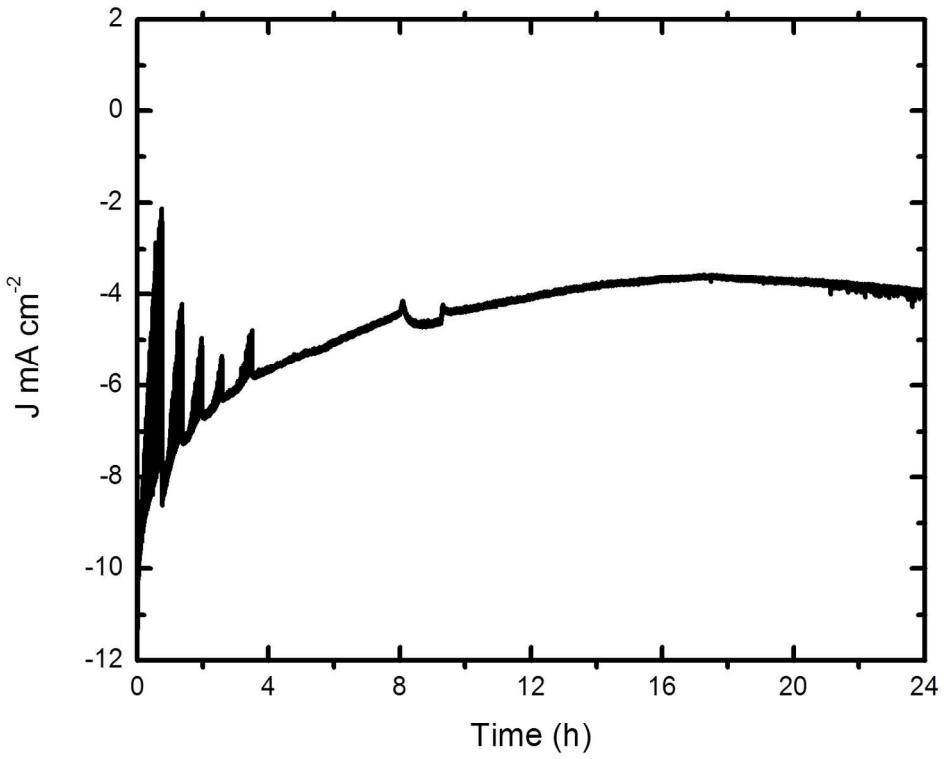

Figure S11. Chronoamperogram of the thin films at an overpotential of 250 mV in 0.1M H_2SO_4 for 24 hours.

	Mo	C	O	Se
As-Deposited	5.10%	61.50%	12.80%	20.50%
After 10 Cycles	2.75%	74.20%	14.80%	8.25%

Table S1. Table of atomic abundances derived from the quantitative analysis of XPS peaks for the as-deposited film and resultant material after 10 potential cycles